

# Calculations of Hartree-Fock polarizabilities for some simple atoms and molecules, and their practicality\*

Vincent P. Gutschick† and Vincent McKoy‡

*Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109*

(Received 11 August 1971)

Hartree-Fock electric polarizabilities have been calculated for  $H_2$ , He, Li, Be, LiH, and  $N_2$ . Perturbation theory with all the coupling terms was employed variationally for the first five, using a variety of basis sets for each. Each basis for the perturbation calculations was composed of a zero-order set, plus a first-order set (appropriate to the direction of polarization, for the molecules). The two sets are disjoint to ensure identical zero-order functions for the two molecular polarizability components and, hence, reliable anisotropy values. Nonorthogonal theory as formulated by Das and Duff [Phys. Rev. **168**, 43 (1968)], assuming exact zero-order orbitals, was used for LiH. For practical reasons, the nitrogen molecule was treated by the fully self-consistent approach which does not distinguish orders of perturbation. The results for all six species are in very good agreement with experiment, reflecting both a reliable choice of polarization functions and, more significantly, the basic accuracy of the Hartree-Fock method for the static charge distributions, both unperturbed and perturbed by an electric field.

## I. INTRODUCTION AND THEORY

Among variational theories of molecular electronic structure, the Hartree-Fock theory has proved particularly valuable for a practical understanding of such properties as chemical binding, electric multipole moments, and x-ray scattering. It provides the most tractable method of calculating first-order properties under external or internal one-electron perturbations, either developed explicitly in orders of perturbation theory or in the fully self-consistent method. Electric polarizabilities,<sup>1-4</sup> and magnetic properties<sup>5</sup> such as spin coupling, chemical shift, and susceptibility have been treated with the theory. The accuracy and consistency of first-order properties are poorer than those of zero-order properties. Most often this is due to use of explicit approximations in solving the first-order perturbation equations, or to the inaccuracies of the zero-order molecular orbitals (MO's) which may undermine the variational principle for the second-order energy. Theoretical studies using many-body theory<sup>6,7</sup> indicate that the Hartree-Fock theory itself is basically sound for static or zero-frequency properties, and we do not intend to draw further conclusions along this line. Rather, we have performed representative calculations of static electric polarizabilities for small atoms and molecules to underscore the basic soundness of perturbed Hartree-Fock theory, giving important and practical guidelines for selecting the variational basis sets for the first-order wavefunction.

Our first studies were on  $H_2$  and the atoms He, Li, Be using a variety of simple wavefunctions constructed from Slater-type orbitals (STO's). For such few-electron species, the problem is best solved by constructing explicit first-order perturbation equations for the perturbation  $\phi_i^1$  to the unperturbed molecular orbitals  $\phi_i^0$ . The unperturbed electronic Hamiltonian contains one-electron terms  $h_i^0$  and two-electron terms  $g_{ij} = 1/r_{ij}$

(in atomic units),

$$H^0 = \sum_i h_i^0 + \sum_{i < j} g_{ij}. \quad (1)$$

The perturbation due to an electric field  $\mathcal{E}$  along the axis  $k$  is

$$H^1 = \mathcal{E} \sum_i h_i^1 = \mathcal{E} \sum_{ik} r_{ik},$$

and the zero-order and first-order Hartree-Fock equations are, respectively,

$$(h^0 + \sum_j \langle \phi_j^0 | \cdot | \phi_j^0 \rangle - \epsilon_i^0) \phi_i^0 = 0, \quad (2a)$$

$$\begin{aligned} & (h^0 + \sum_j \langle \phi_j^0 | \cdot | \phi_j^0 \rangle - \epsilon_i^0) \phi_i^1 \\ & + (h^1 + \sum_j [\langle \phi_j^1 | \cdot | \phi_j^0 \rangle + \langle \phi_j^0 | \cdot | \phi_j^1 \rangle] - \epsilon_i^1) \phi_i^0 = 0, \end{aligned} \quad (2b)$$

with the usual convention of order-by-order orthogonality,

$$\langle \phi_i^0 | \phi_j^0 \rangle = \delta_{ij}, \quad (3a)$$

$$\langle \phi_i^0 | \phi_j^1 \rangle = 0. \quad (3b)$$

Here we use the shorthand notation

$$\langle a | \cdot | b \rangle c = \langle a(j) | g_{ij} | b(j) \rangle c(i) - \langle a(j) | g_{ij} | c(j) \rangle b(i). \quad (4)$$

The zero-order equation is commonly solved variationally using STO's ( $\chi_p^0$ ) centered on the nuclei,

$$\phi_i^0 = \sum_p c_{ip}^0 \chi_p^0. \quad (5)$$

The first-order equation may be solved variationally in a similar way. Operationally, this means making Eq. (2b) hold for all projections with the first-order basis

set  $\{\chi^1\}$ ,

$$\langle \chi_p^1 | h^0 + \sum_j \langle \phi_j^0 | \cdot | \phi_j^0 \rangle - \epsilon_i^0 | \phi_i^1 \rangle + \langle \chi_p^1 | h^1 + \sum_j [\langle \phi_j^0 | \cdot | \phi_j^1 \rangle + \langle \phi_j^1 | \cdot | \phi_j^0 \rangle] - \epsilon_i^1 | \phi_i^0 \rangle = 0 \quad (6)$$

for all  $p$  and  $i$ . Substitution of the appropriate basis expansions for the  $\phi_i^1$ , including the explicit forms for the matrix elements  $\epsilon_i^1$ , yields linear equations for the first-order coefficients  $c_{ip}^1$ . This is equivalent to minimizing the second-order energy, *assuming* the exactness of the zero-order solution in the *total* basis  $\{\chi\} = \{\chi^0\} + \{\chi^1\}$ ,

$$\langle \chi_r | h^0 + \sum_j \langle \phi_j^0 | \cdot | \phi_j^0 \rangle - \epsilon_i^0 | \phi_i^0 \rangle = 0 \quad (7)$$

for all  $r$ .

Given a zero-order basis  $\{\chi^0\}$  and the direction or axis of polarization  $k$ , the polarization functions  $\{\chi^1\}_k$  can be picked judiciously to include all important shifts in orbital amplitudes while remaining few in number. A major part of the work reported herein concerns just such a choice of the basis. We have shown that the distortion of  $\phi_i^0$  can be adequately described by allowing each atomic orbital in the MO to distort in the electric field as a pure hydrogenic orbital would distort. For the  $H_2$  molecule and the three atoms He, Li, Be, our work is further simplified since the polarization functions are automatically of a different symmetry from the occupied orbitals:  $\sigma_u$  vs  $\sigma_g$  for  $H_2$  and  $p$  vs  $s$  for the atoms. The calculations proceed very straightforwardly to the second-order energy in the electric field,

$$\mathcal{E}^2 E^{(2)} = \mathcal{E}^2 \sum_i \langle \phi_i^1 | h^1 | \phi_i^0 \rangle, \quad (8a)$$

which directly measures the polarizability as

$$E^{(2)} = -\frac{1}{2}\alpha. \quad (8b)$$

We obtained excellent agreement with most reliable values, either experimental or theoretical. The results were markedly insensitive to the choice of zero- and first-order bases.

We were encouraged to try molecules of low symmetry and more electrons. The first case was LiH, previously treated by Lipscomb and Stevens<sup>1</sup> in similar fashion. Now our simple expedient of distorting the atomic orbital basis functions as if they described hydrogenic atoms yields a first-order basis composed of functions *not* automatically orthogonal to the occupied orbitals by symmetry. We can Schmidt orthogonalize the  $\chi_p^1$  to the  $\chi_q^0$  before doing any perturbation calculations, but this involves much manipulation of the raw one- and two-electron integrals over basis functions. The nonorthogonal perturbation formalism of Das and Duff<sup>8</sup> performs instead a symmetric deorthogonalization in the matrix equations (6). They perform the deorthogonalization *before* separating orders of perturbation in the Hartree-Fock equations and minimizing the second-order energy with respect to

the  $\phi_i^1$ . Thus, they obtain extra terms in the first-order equation due to inexactness of the  $\phi_i^0$  in the augmented basis  $\{\chi^0\} + \{\chi^1\}_k$ : Eq. (7) is not satisfied. Most often these terms are small and can be dropped much as Das and Duff do in their final presentation. We then have at hand a formalism for computing separately the two polarizability components  $\alpha_k$  ( $\alpha_{zz}$  and  $\alpha_{xx}$ ) in small total bases while retaining reliability of the anisotropy  $\alpha_k - \alpha_l$ .

Finally we tried the  $N_2$  molecule, with its many electrons and many occupied symmetry types of orbitals. Practical zero-order bases of Gaussian-type orbitals (GTO's) do *not* keep the  $\phi_i^0$  inexactness terms in the perturbation equations sufficiently small any more. Even in LiH, GTO's cause this problem. The inexactness terms are too prolific to include. The problem is avoided by shifting both zero- and first-order calculations to the common, enlarged basis  $\{\chi^0\} + \{\chi^1\}_k$ . The unoccupied virtual orbitals from zero order can then act as the new  $\chi_p^1$ . To once more avoid much manipulating of two-electron integrals, we abandoned the perturbation formalism in favor of the fully self-consistent approach, equivalent at low fields<sup>8</sup>. The basic Hartree-Fock equations unseparated into orders are solved, given a finite electric field. The field is small enough such that  $\phi_i \approx \phi_i^0 + \phi_i^1$  and  $E \approx E^0 + \mathcal{E}E^{(1)} + \mathcal{E}E^{(2)}$  and higher orders are negligible (for  $N_2$ ,  $E^{(1)} = 0$ , too). Now, if one computed the two polarizability components separately, the anisotropy  $\alpha_k - \alpha_l$  would be less reliable because the unperturbed energy is doubtlessly shifted differently in the two different *total* bases  $\{\chi^0\} + \{\chi^1\}_k$ ,  $\{\chi^0\} + \{\chi^1\}_l$ . We thus prefer one large basis  $\{\chi^0\} + \{\chi^1\}_k + \{\chi^1\}_l$  for all calculations. Fortunately, for  $N_2$  a good zero-order basis  $\{\chi^0\}$  already contains many functions which may also act as polarization functions and  $\{\chi^0\}$  is not greatly enlarged by adding the nonredundant parts of  $\{\chi^1\}_k$  and  $\{\chi^1\}_l$ .

Beyond the approximation of finite basis expansion for the molecular orbitals  $\phi_i$  (in all orders), several approximations to Hartree-Fock theory have been proposed. The explicit perturbation equations (2b) are altered in these approximations to eliminate the need for all or most of the two-electron integrals over basis functions. Dalgarno<sup>9</sup> has discussed these methods, and the approximations have been evaluated relative to the "full theory" by Langhoff, Karplus, and Hurst.<sup>10</sup> While these theories save most of the effort in evaluating a first-order property, they consistently undervalue the polarizability to an unpredictable extent. We wish to test the accuracy of full Hartree-Fock theory which neglects only instantaneous correlation. We do not consider further the approximations to its perturbation formalism.

## II. APPLICATIONS AND RESULTS

Many polarizability, magnetic susceptibility, and magnetic shielding calculations have been done for  $H_2$ ,

TABLE I. Polarizability of H<sub>2</sub> for various wavefunctions.

	<i>R</i>	STO bases { $\chi^0$ }, { $\chi^1$ } <sup>a</sup> for Hartree-Fock (HF) or valence bond (VB) wavefunctions	$\alpha_{  }$ (% error) <sup>b</sup>	$\alpha_{\perp}$ (% error)
A	1.402	{0} = 1s (1.197) HF {1} = 2p, 3p (1.197)	6.345(−1.0)	4.238(−7.5)
B	1.406	{0} = 1s (1.166) VB {1} = 2p, 3p (1.166)	6.003(−7.1)	4.441(−3.4)
C		{1} = 2p, 3p (1.100)		4.469(−2.8)
D	1.402	{0} = 1s (1.378), 2s (1.176) 2p (1.820) HF {1} = 2p, 3p (1.378)	6.090(−4.9)	4.102(−10.5)
E		{1} = 2p, 3p (1.378) 2p, 4p (1.176)	6.321(−1.3)	4.597(+2.9)

<sup>a</sup> First-order bases are constrained as linear combinations by the solution of Eq. (10) (see text).

<sup>b</sup> Error is relative to the accurate theoretical values of Ref. 14 (see text). Accurate values of ( $\alpha_{||}$ ,  $\alpha_{\perp}$ ) are (6.407, 4.584) at  $R=1.402$  and (6.460, 4.597) at  $R=1.406$ . All values are atomic units (a.u.),  $a_0^3$ .

by all manners of perturbation theory and with all types of unperturbed wavefunctions. We focused on the simpler zero-order wavefunctions, the Coulson<sup>11</sup> and Ransil<sup>12</sup> Hartree-Fock (HF) functions, and the Wang<sup>13</sup> valence-bond (VB) function. The Coulson and Wang wavefunctions use only one 1s atomic orbital on each center, while the Ransil function includes one 2s and one 2p<sub>z</sub> in addition. In each case the wavefunction was perturbed by letting each basis function  $\chi_p^0$  assume the variational form (there is only one MO),

$$\chi_p \rightarrow \chi_p^0 + c\epsilon\chi_p^1, \quad (9)$$

with  $c$  a variational constant. For the two HF wavefunctions this is equivalent to the perturbed HF formalism outlined previously,

$$\phi_i \rightarrow \phi_i^0 + \epsilon\phi_i^1.$$

The analogous VB treatment involves straightforward minimization of the second-order energy.

The  $\chi_p^1$  were selected initially as solutions of the hydrogenlike atom in an electric field with  $\chi_p^0$  as the unperturbed wavefunction,

$$\left[-\frac{1}{2}\nabla^2 - (Z/r) + (Z^2/2n_p^2)\right]\chi_p^1 + (-\zeta_p r_k - \epsilon_{pk}^1)\chi_p^0 = 0. \quad (10)$$

Here  $n_p$  is the principal quantum number of  $\chi_p^0$ ,  $\zeta_p$  is the orbital exponent,  $Z$  is the effective nuclear charge  $n_p\zeta_p$ , and  $\epsilon_{pk}^1$  is the first-order energy associated with the perturbation  $-\epsilon r_k$  along the Cartesian axis  $k$ . Thus a 1s STO in a  $z$ -directed field yields as  $\chi_p^1$  a linear combination of 2p<sub>z</sub> and 3p<sub>z</sub> of the same  $\zeta_p$ ; a 2s Slater—a 2p<sub>z</sub>, 3p<sub>z</sub>, and 4p<sub>z</sub> combination; a 2p<sub>x</sub>—a 3d<sub>xx</sub> and 4d<sub>xx</sub>; a 2p<sub>y</sub>—a 1s, 2s, 3s, 4s, 3d<sub>yz</sub>— $r^2$ , and 4d<sub>yz</sub>— $r^2$ . All of the hydrogen molecule trials used the STO's in the  $\chi_p^1$  frozen in their original linear combinations, even if, for

example, only 2p<sub>z</sub> and 4p<sub>z</sub> were used for the 2s polarization. The molecular calculations on LiH and N<sub>2</sub> in contrast used Eq. (10) simply as an indication of important primitive basis functions, STO or GTO, to include in bases unconstrained by any linear combinations.

The results are in Table I. Trials A, B, and E are most relevant, as they compare three different simple wavefunctions under essentially complete polarization according to Eq. (11). They are compared to the extremely accurate polarizabilities of Kołos and Wolniewicz<sup>14</sup> who used a 54-term zero-order wavefunction and 34 terms in first order. Quadratic interpolation was done to the internuclear distances  $R$  used in our calculations. Sufficiently accurate experimental polarizabilities are only available at optical frequencies. The insensitivity of our results to the choice of the zero-order functions along with the first-order wavefunction chosen according to Eq. (11), and their agreement with experiment are very encouraging. Result C shows that optimization of the exponents for polarization functions is unnecessary, and case D indicates a need for polarizing the majority of the zero-order basis.

The He, Li, and Be atoms were treated next, using Clementi's<sup>15</sup> unperturbed wavefunctions computed in double-zeta basis sets. An accurate He polarizability,  $\alpha = 1.397$  a.u., has been obtained by Johnston *et al.*<sup>16</sup> by extrapolation of the experimental dielectric constant to zero pressure. Dutta *et al.*<sup>17</sup> have used many-body theory on He and found  $\alpha = 1.407$  a.u. Our result of 1.319 a.u. is 6.0% low relative to the experiments, the first in a trend to undervaluing the correct polarizability for atoms. The true Li polarizability is probably in the range 160–170 a.u. The most precise measurement<sup>18a</sup> is on bulk lithium metal, using Stark splitting, and it yields  $\alpha = 182$  a.u. Atomic-beam deflection experiments

are far less precise but do involve *isolated* atoms as we wish. The best value<sup>18b</sup> among these is  $148 \pm 14$  a.u., but this is probably too low.<sup>18b, 18c</sup> Our Li wavefunction, which is of unrestricted Hartree-Fock form, gave a result of 167.6 a.u., 7.9% below the experimental value of 182 a.u. The beryllium atom provided our greatest success, as it has for several other calculations using Hartree-Fock theory; the computed value of 45.28 a.u. lies only 3.2% lower than the accurate many-body result of 46.77 a.u. due to Kelly.<sup>7</sup> No experimental results are reliable. All three atomic calculations showed negligible, usually negative contributions to  $\alpha$  by the core orbitals, as might be expected.

The LiH molecule, as a heteronuclear species with two electronic shells, provides a somewhat better test of Hartree-Fock theory, particularly its nonorthogonal formulation discussed in the previous section. Ransil's<sup>19</sup> wavefunction was chosen for zero order at the experimental internuclear distance  $R = R_e = 3.015$  a.u. The perpendicular polarization was represented by the full set of four hydrogenic-model polarization functions  $\chi_p$ —see Eq. (11). Standard orthogonal perturbation theory<sup>20</sup> could be used for  $\alpha_{\perp}$ , yielding the value 26.22 a.u. This agrees well with the most reliable theoretical estimate of 27.00 a.u. by Stevens and Lipscomb.<sup>1</sup> The parallel component is more difficult, requiring non-orthogonal theory. We chose to test here many of our ideas on the adequacy of polarization functions, and so we pooled all 13 primitive  $\chi_p$  as unconstrained individual STO's, plus the two virtuals from zero order. The complete basis yielded  $\alpha_{\parallel} = 25.29$ . Stevens and Lipscomb<sup>1</sup> did not compute  $\alpha_{\parallel}$  because of the change of zero-order basis necessary to retain the orthogonal perturbation theory. Kolker and Karplus<sup>2</sup> have made cruder calculations,  $\alpha_{\parallel} = 25.38$  a.u. and  $\alpha_{\perp} = 34.42$  a.u., which are in poor agreement with ours, but at least show a negative anisotropy  $\alpha_{\parallel} - \alpha_{\perp} = -9.04$  a.u.; our value is  $-0.93$  a.u. We could conclude that the  $2p$ ,  $3p$ -like orbitals from polarization of the tight  $1s_{\text{Li}}$ , the  $2p$  from the  $2s_{\text{Li}}$  (nearly redundant with the zero-order  $2p$ ), and the  $2s$  from the  $2p_{\text{Li}}$  polarization were all unimportant. This new basis  $\{\chi^1\}$  yielded  $\alpha_{\perp} = 25.04$  to confirm our judgment. Many other deletions were tried, with a nine-function set being the smallest to give a good result: the two virtuals plus the  $3p$ ,  $4p$  STO's from the  $2s_{\text{Li}}$ , the  $1s$ ,  $3s$ ,  $3d$  from the  $2p_{\text{Li}}$ , and the  $2p$ ,  $3p$  from the  $2s_{\text{H}}$  gave  $\alpha_{\parallel} = 24.63$  a.u. In all these calculations the inner core orbital was seen to back-polarize slightly, following the trend of the atoms.

The  $\text{N}_2$  molecule is tractable only in a Gaussian basis set due to the large number of two-center, two-electron integrals required. For experience in selecting the  $\{\chi_p^1\}$ , we returned to the LiH molecule in a GTO basis. We attempted to reproduce the nonorthogonal perturbation theory results for STO's, choosing Gaussians contracted by Huzinaga's<sup>21</sup> prescription to mimic the STO's for atoms. While the zero-order energy was close, the dipole

moment was poorer and the polarizability using just the two virtual orbitals was two-thirds that obtained using the STO's. This indicates poor tails for the Gaussian wavefunctions. We tried to add to the non-orthogonal perturbation theory the extra terms due to inexactness of the  $\phi_i^0$ , but these proliferated wildly. Instead we settled for an equivalent fully self-consistent approach discussed earlier. The polarizability is taken from the ratio of the induced dipole moment to the electric field, possibly extrapolated to zero field for greater accuracy. We did not do such extrapolations, since the larger inherent error of Hartree-Fock theory does not warrant it.

We began our LiH calculations with a very large basis of  $zz$  functions covering a full range of exponents in  $1s$ ,  $2p$ , and  $3d$  GTO's for Li and  $1s$ ,  $2p$  for H. By trial and error we pared the basis to 15 functions, which yielded  $\alpha_{\parallel} = 21.06$ ,  $\alpha_{\perp} = 22.56$ . The anisotropy is negative as for STO's, but absolute magnitudes are down about 15%, somewhat disturbingly. Perhaps lack of closely spaced exponents for the Gaussians is responsible, as this disallows construction of more diffuse functions with radial nodes.

Proceeding to  $\text{N}_2$ , we built from the zero-order basis of Dunning<sup>22</sup> consisting of 13 contracted GTO's (22 primitives) on each nitrogen, four of the  $s$  type, three of each  $p$  component. The calculations were done at the experimental internuclear distance, 2.068 a.u. We added on each center a diffuse  $1s$  ( $\zeta = 0.0800$ ) for  $z$  polarization of the  $2p_z$  or  $x$  polarization of the  $2p_x$ ; a similarly diffuse  $2p$  (0.0800) of all three directions for  $x$  and  $z$  polarizations of the  $\sigma$  orbitals; and a host of  $d$  functions all of moderately diffuse exponent 0.200. Among the  $d$  functions the two-center linear combination  $XX_A + XX_B$  covers the  $x$  field on  $\pi_u^x$  orbital;  $YY_A + YY_B$  is simply the complement to the above for the  $\sigma$ -orbital balance;  $XY_A + XY_B$  covers the  $x$  field on  $\pi_u^y$ , while  $YZ_A + YZ_B$  is for the  $z$  field;  $XZ_A$  and  $XZ_B$  are used independently to represent the  $x$  polarization of  $\sigma_g$ ,  $\sigma_u$  and the  $z$  polarization of the  $\pi_u^x$  orbital.

The computed  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are 14.97 and 9.46 a.u., respectively. It is of practical interest that it was extremely difficult to obtain convergence of the SCF procedure for the  $z$ -polarized case. Three-point extrapolation<sup>23</sup> by the  $e_k$  procedure for oscillating and diverging series was used, as outlined by Petersson and McKoy.<sup>23</sup> The comparable experimental values are  $\alpha_{\parallel} = 16.06$  and  $\alpha_{\perp} = 9.78$  a.u. obtained dynamically with Na  $D$  light.<sup>24</sup> Dispersion corrections may be estimated to give static polarizabilities of 15.9 and 9.7 a.u. The agreement of theory and experiment is quite remarkable. It may be partly fortuitous, due to a 5%–15% underestimation of  $\alpha$  when using a GTO basis, or to increased inaccuracy of the highly polarizable valence orbitals in systems of many electrons. One more interesting feature of the  $\text{N}_2$  polarization is the coupling of orbitals in pairs under the field influence. The  $1\sigma_g$ ,  $1\sigma_u$  orbitals are essentially

unpolarized for both field directions. For an  $x$  field, the  $2\sigma_g$  gives 11.4% of the polarizability and the  $2\sigma_u$  31.0%; the  $3\sigma_g$  and  $1\pi_u^x$  couple, with the latter antipolarizing, to give another 42.4%; and the  $1\pi_u^y$  yields the last 15.2%. In a  $z$  field the  $2\sigma_g$  contributes 4.1%; the  $2\sigma_u$ - $3\sigma_g$  coupled give 26.0%; the  $1\pi_u^x$  31.1%; and the  $1\pi_u^y$  38.8%. The disparity of the last two contributions is due to a slight inequivalence in the zero-order descriptions of the two orbitals: the  $xz_A$ ,  $xz_B$  polarization functions also enter into the unperturbed  $1\pi_u^z$ .

### III. CONCLUSIONS

Hartree-Fock theory for the static first-order property of polarizability appears adequate when solved exactly within a modest basis, under quite general circumstances of molecular structure and of basis set composition. The smallness of electron correlation effects has been previously displayed explicitly with many-body theory<sup>6,7</sup> in special cases, and the work reported here supports this conclusion more widely. Hartree-Fock theory may give poor electronic excitation frequencies, but at all perturbing field frequencies low relative to correlation processes for virtual or real excitations it does well for properties. The model should be useful for calculating such experimentally inaccessible properties as molecular polarizabilities in their dependence on internuclear distance,  $\alpha(R)$ . The variation of the polarizability of a pair of atoms as a function of distance has well-defined effects, including increased cross section for vibrational excitation in electron-molecular collisions, strong contribution to the second dielectric virial coefficient,<sup>25</sup> collision-induced light scattering,<sup>26</sup> and a nonlinear refractive index.<sup>27</sup> Of course, one must be careful in using molecular Hartree-Fock wavefunctions far from equilibrium internuclear separations  $R_e$ : For molecules dissociating into fragments with unclosed shells, the Hartree-Fock wavefunction is incorrect except near  $R_e$ . Multiconfiguration self-consistent field calculations can remedy this fault while increasing the computing effort; the fully self-consistent approach to polarizabilities remains viable in this framework.

### ACKNOWLEDGMENTS

The authors would like to thank David Huestis, Jeffrey Hay, Robert Ladner, Woodrow Wilson, Thomas Dunning, Richard Blint, William A. Goddard III, and Luis Kahn for help with computer programming. We had many helpful discussions on theory with Thomas Dunning and William A. Goddard III. Tara P. Das provided much help in clarifying points about nonorthogonal perturbation theory.

\* Contribution No. 4313.

† National Science Foundation Predoctoral Fellow, 1966-1970.

‡ Alfred P. Sloan Foundation Fellow.

<sup>1</sup> R. M. Stevens and W. N. Lipscomb, *J. Chem. Phys.* **40**, 2238 (1964).

<sup>2</sup> H. J. Kolker and M. Karplus, *ibid.* **39**, 2011 (1963).

<sup>3</sup> V. G. Kaveeshar, K. T. Chung, and R. P. Hurst, *Phys. Rev.* **172**, 35 (1968).

<sup>4</sup> G. P. Arrighini, M. Maestro, and R. Moccia, *Chem. Phys. Letters* **1**, 242 (1967).

<sup>5</sup> H. F. Hameka, *Advanced Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1965).

<sup>6</sup> T. C. Caves and M. Karplus, *J. Chem. Phys.* **50**, 3649 (1969).

<sup>7</sup> H. P. Kelly, *Phys. Rev.* **136**, B896 (1964).

<sup>8</sup> T. P. Das and K. J. Duff, *Phys. Rev.* **168**, 43 (1968).

<sup>9</sup> A. Dalgarno, *Advan. Phys.* **11**, 281 (1962); with J. M. McNamee, *J. Chem. Phys.* **35**, 1517 (1961).

<sup>10</sup> P. W. Langhoff, M. Karplus, and R. P. Hurst, *J. Chem. Phys.* **44**, 505 (1966).

<sup>11</sup> C. A. Coulson, *Trans. Faraday Soc.* **33**, 1479 (1937).

<sup>12</sup> B. J. Ransil, *J. Chem. Phys.* **35**, 1967 (1961).

<sup>13</sup> S. Wang, *Phys. Rev.* **31**, 579 (1928).

<sup>14</sup> W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **46**, 142 (1967).

<sup>15</sup> E. Clementi, IBM Research Paper RJ-256, 6 August 1963.

<sup>16</sup> D. A. Johnston, C. J. Oudemans, and R. H. Cole, *J. Chem. Phys.* **33**, 1310 (1960).

<sup>17</sup> N. C. Dutta, T. Ishihara, C. Matsubara, and T. P. Das, *Phys. Rev. Letters* **2**, 8 (1969).

<sup>18</sup> (a) E. Fues, *Z. Physik* **82**, 536 (1933); (b) G. W. Chamberlain and J. C. Zorn, *Phys. Rev.* **129**, 677 (1963); (c) M. R. Flannery and A. L. Stewart, *Proc. Phys. Soc. (London)* **82**, 188 (1963).

<sup>19</sup> B. J. Ransil, *Rev. Mod. Phys.* **32**, 245 (1960).

<sup>20</sup> R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb, *J. Chem. Phys.* **38**, 550 (1963).

<sup>21</sup> S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

<sup>22</sup> T. H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970).

<sup>23</sup> P. Wynn, *Math. Aids Computation* **54**, 91 (1956); G. A. Petersson and V. McKoy, *J. Chem. Phys.* **46**, 4362 (1967).

<sup>24</sup> A. A. Maryott and F. Buckley, *Natl. Bur. Stds. (U.S.) Circular* **537** (1953).

<sup>25</sup> See, e.g., T.-K. Lim, B. Linder, and R. A. Kromhout, *J. Chem. Phys.* **52**, 3831 (1970).

<sup>26</sup> J. P. McTague and G. Birnbaum, *Phys. Rev.* **3**, 1376 (1971).

<sup>27</sup> J. P. McTague, C. H. Lin, T. Gustafson, and R. Chiao, *Phys. Letters* **A32**, 82 (1970).